

10/568,388

EAST Search History

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	998	(556/136).CCLS.	US-PGPUB; USPAT; EPO; JPO	OR	OFF	2007/04/19 17:17
L2	796	(427/252).CCLS.	US-PGPUB; USPAT; EPO; JPO	OR	OFF	2007/04/19 17:17

10/568,388

(FILE 'HOME' ENTERED AT 13:11:26 ON 19 APR 2007)

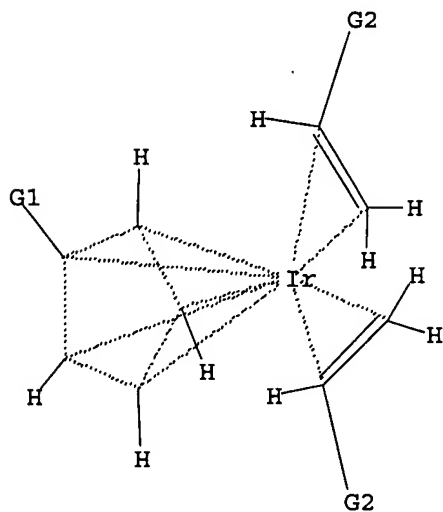
FILE 'REGISTRY' ENTERED AT 13:11:46 ON 19 APR 2007

L1 STRUCTURE UPLOADED

=> d l1

L1 HAS NO ANSWERS

L1 STR



G1 Me,Et,n-Pr,i-Pr,n-Bu,i-Bu,s-Bu,t-Bu

G2 Me,Et,n-Pr,i-Pr,n-Bu,i-Bu,s-Bu,t-Bu,H

Structure attributes must be viewed using STN Express query preparation.

=> s l1

SAMPLE SEARCH INITIATED 13:12:35 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 4082 TO ITERATE

49.0% PROCESSED 2000 ITERATIONS

0 ANSWERS

INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**

BATCH **COMPLETE**

PROJECTED ITERATIONS: 77809 TO 85471

PROJECTED ANSWERS: 0 TO 0

L2 0 SEA SSS SAM L1

=> s l1 full

FULL SEARCH INITIATED 13:12:42 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 81747 TO ITERATE

100.0% PROCESSED 81747 ITERATIONS

2 ANSWERS

SEARCH TIME: 00.00.01

L3 2 SEA SSS FUL L1

=> fil caplus

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

172.55

172.76

FILE 'CAPLUS' ENTERED AT 13:12:48 ON 19 APR 2007
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FILE COVERS 1907 - 19 Apr 2007 VOL 146 ISS 17
FILE LAST UPDATED: 18 Apr 2007 (20070418/ED)

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=> s 13

L4 2 L3

=> d 1-2 bib abs

L4 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2007 ACS on STN

AN 2006:1092415 CAPLUS

DN 146:37159

TI Fabrication of Ir-based electrodes by metal organic chemical vapor deposition using liquid Ir precursors

AU Fujisawa, Hironori; Watari, Soichi; Iwamoto, Naoya; Shimizu, Masaru; Furukawa, Taishi; Kawano, Kazuhisa; Oshima, Noriaki

CS Department of Electrical Engineering and Computer Sciences, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo, 671-2201, Japan

SO Japanese Journal of Applied Physics, Part 1: Regular Papers, Brief Communications & Review Papers (2006), 45(9B), 7354-7359
CODEN: JAPNDE

PB Japan Society of Applied Physics

DT Journal

LA English

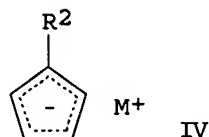
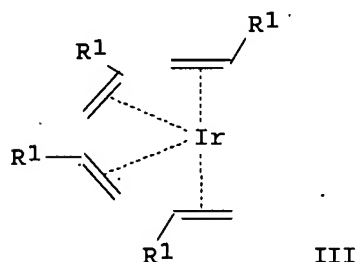
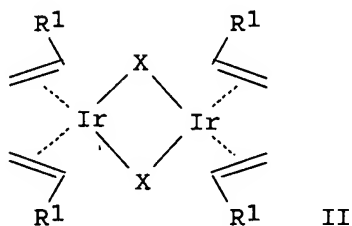
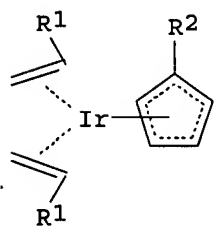
AB Ir-based electrodes were fabricated by metal organic CVD (MOCVD) using a newly developed liquid precursor, (ethylcyclopentadienyl)bis(ethylene)iridium $[\text{Ir}(\text{EtCp})(\text{C}_2\text{H}_4)_2]$, with a lower decomposition temperature than previous precursors, (ethylcyclopentadienyl)(1,5-cyclooctadiene) iridium $[\text{Ir}(\text{EtCp})(\text{COD})]$ and (ethylcyclopentadienyl)(1,3-cyclohexadiene) iridium $[\text{Ir}(\text{EtCp})(\text{CHD})]$. Film growth behavior during MOCVD using $\text{Ir}(\text{EtCp})(\text{C}_2\text{H}_4)_2$ was studied and compared with that using $\text{Ir}(\text{EtCp})(\text{COD})$ and $\text{Ir}(\text{EtCp})(\text{CHD})$. When $\text{Ir}(\text{EtCp})(\text{C}_2\text{H}_4)_2$ was used, significantly higher nucleation was observed at the initial growth stage than that using $\text{Ir}(\text{EtCp})(\text{COD})$ and $\text{Ir}(\text{EtCp})(\text{CHD})$ owing to the lower thermal decomposition temperature of 220°. Ir, IrO₂ and Ir/IrO₂ films were successfully prepared using $\text{Ir}(\text{EtCp})(\text{C}_2\text{H}_4)_2$ on underlying SiO₂, TiN and Pb(Zr,Ti)O₃, showing that Ir-based top and bottom electrodes can be fabricated by MOCVD. The root-mean-square surface roughnesses and elec. resistivities of Ir and IrO₂ films on SiO₂ were 2.2 nm and 9.4 μΩ cm, and 3.3 nm and 1.8 + 102 μΩ cm, resp. The step coverage of Ir films prepared at 230-400° were 35-45%.

RE.CNT 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD

ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2007 ACS on STN
 AN 2005:161097 CAPLUS
 DN 142:261654
 TI Organoiridium compound, process for producing the same, and process for producing film
 IN Kawano, Kazuhisa; Takamori, Mayumi; Oshima, Noriaki
 PA Tosoh Corporation, Japan; Sagami Chemical Research Center
 SO PCT Int. Appl., 17 pp.
 CODEN: PIXXD2
 DT Patent
 LA Japanese
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 2005017950	A2	20050224	WO 2004-JP11796	20040811
	WO 2005017950	A3	20050331		
	W:				
	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
	RW:				
	BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
	JP 2005225855	A	20050825	JP 2004-191388	20040629
	EP 1657245	A2	20060517	EP 2004-771757	20040811
	R: DE, FR, GB				
	CN 1835961	A	20060920	CN 2004-80023620	20040811
	US 2006204660	A1	20060914	US 2006-568388	20060215
PRAI	JP 2003-295329	A	20030819		
	JP 2003-383169	A	20031112		
	JP 2004-5503	A	20040113		
	WO 2004-JP11796	W	20040811		
OS	MARPAT 142:261654				
GI					



AB There are provided an organoiridium compound represented by the general formula (I) ($R_1 = H$, lower alkyl; $R_2 =$ lower alkyl) which has a low m.p. and excellent vaporization characteristics, exhibit thermal decomposition at lower temperature compared to existing material, and can deposit a film on substrates at low temps.; and a process for producing an iridium-containing film from the organometallic compound. A compound represented by the general formula (II) or the general formula (III) (wherein $R_1 =$ same as above; $X =$ halo) is reacted with a compound represented by the general formula (IV) ($R_2 =$ same as above; $M =$ alkali metal) to obtain an organoiridium compound I, e.g., (ethylcyclopentadienyl)bis(ethylene)iridium (V). This compound is used as a raw material to produce an iridium-containing film having excellent step coverage property by chemical vapor deposition process. Thus, 49 mg di(μ -chloro)tetrakis(ethylene)diiridium(I) was added to 10 mL THF, cooled to -78° , treated with a solution of 17 mg lithium ethylcyclopentadienide in 10 mL, stirred at -78° for 30 min, warmed to room temperature, allowed to react for 1 h, concentrated to a muddy mixture, and extracted with hexane to give, after alumina chromatog. of the hexane extract, 14 mg V. V was used to deposit 300 nm iridium film on 100 nm SiO_2 film-coated silicon substrate using N carrier gas and O as oxidizing gas at 400° substrate temperature and 10 Torr.

10/568,388

(FILE 'HOME' ENTERED AT 12:56:30 ON 19 APR 2007)

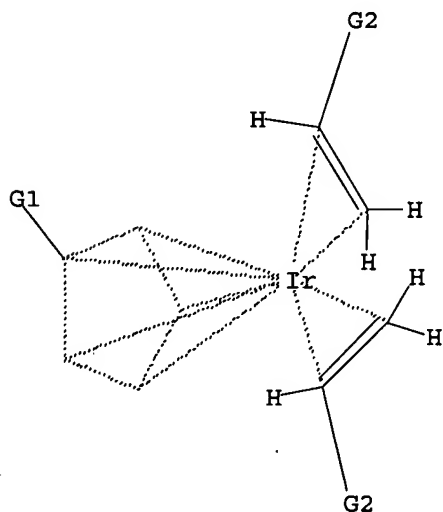
FILE 'REGISTRY' ENTERED AT 12:57:17 ON 19 APR 2007

L1 STRUCTURE UPLOADED

=> d l1

L1 HAS NO ANSWERS

L1 STR



G1 Me,Et,n-Pr,i-Pr,n-Bu,i-Bu,s-Bu,t-Bu

G2 Me,Et,n-Pr,i-Pr,n-Bu,i-Bu,s-Bu,t-Bu,H

Structure attributes must be viewed using STN Express query preparation.

=> s l1

SAMPLE SEARCH INITIATED 12:58:01 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 4082 TO ITERATE

49.0% PROCESSED 2000 ITERATIONS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.01

1 ANSWERS

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**

PROJECTED ITERATIONS: 77809 TO 85471
PROJECTED ANSWERS: 1 TO 125

L2 1 SEA SSS SAM L1

=> s l1 full

FULL SEARCH INITIATED 12:58:06 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 81747 TO ITERATE

100.0% PROCESSED 81747 ITERATIONS
SEARCH TIME: 00.00.01

24 ANSWERS

L3 24 SEA SSS FUL L1

=> fil caplus

COST IN U.S. DOLLARS

FULL ESTIMATED COST

SINCE FILE
ENTRY
172.55

TOTAL
SESSION
172.76

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FILE COVERS 1907 - 19 Apr 2007 VOL 146 ISS 17
FILE LAST UPDATED: 18 Apr 2007 (20070418/ED)

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=> s 13

L4 31 L3

=> s 14 and py<=2003

23917454 PY<=2003

L5 28 L4 AND PY<=2003

=> d 1-28 bib abs

L5 ANSWER 1 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 2003:47783 CAPLUS

DN 138:401869

TI Half-sandwich-type complexes of iridium with tetramethylcyclopentadienyl as ligand

AU Mahr, A.; Nurnberg, O.; Werner, H.

CS Inst. fuer Anorganische Chemie der Universitat, Wurzburg, Germany

SO Zeitschrift fuer Anorganische und Allgemeine Chemie (2003), 629(1), 91-98

CODEN: ZAACAB; ISSN: 0044-2313

PB Wiley-VCH Verlag GmbH & Co. KGaA

DT Journal

LA German

OS CASREACT 138:401869

AB The Ir(I) complexes $[(\eta^5\text{-C}_5\text{HMe}_4)\text{Ir}(\text{C}_2\text{H}_4)_2]$ and $[(\eta^5\text{-C}_5\text{HMe}_4)\text{Ir}(\text{CO})_2]$, which were prepared from $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ or $[\text{IrCl}(\text{CO})_3]\text{n}$ and LiC_5HMe_4 , react with tosyl chloride as well as with X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{iodo}$) by oxidative addition to yield the corresponding Ir(III) compds. Treating $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrX}_2]\text{n}$ ($\text{X} = \text{Cl } 7, \text{Br } 8, \text{iodo } 9$) with CO or PR_3 ($\text{R} = \text{Me}, \text{Ph}$) leads to cleavage of the halide bridges and to the formation of mononuclear $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrX}_2(\text{CO})]$ ($\text{X} = \text{Br}, \text{iodo}$) and $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrX}_2(\text{PR}_3)]$ ($\text{X} = \text{Cl}, \text{Br}, \text{iodo}; \text{R} = \text{Me}, \text{Ph}, \text{i-Pr}, \text{tert-Bu}$), resp. The mol. structure of $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrBr}_2(\text{PiPr}_3)]$ was determined crystallog., [monoclinic, space group $\text{P}2_1/\text{n}$, a 9.4150(10), b 12.896(2), c 17.181(2) Å, β 92.490(9)°, $Z = 4$]. The reactions of 8 and 9 with $\text{Ph}_2(\text{CH}_2)\text{nPPH}_2$ ($\text{n} = 1$ or 2) afford the bridged compds. $\{[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrX}_2]_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)\text{nPPH}_2\}\}$ ($\text{X} = \text{Br}, \text{iodo}; \text{n} = 1, 2$). The dihalide complexes $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrI}_2(\text{PPh}_3)]$ and $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrX}_2(\text{PiPr}_3)]$ ($\text{X} = \text{Cl}, \text{Br}, \text{iodo}$) react with hydride sources to give the dihydrido- and monohydrido derivs. $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrH}_2(\text{PPh}_3)]$

and $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrH}(\text{X})(\text{PiPr}_3)]$ ($\text{X} = \text{Cl}, \text{Br}, \text{iodo}$). The related di-Me and monomethyl compds. $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrMe}_2(\text{PiPr}_3)]$ and $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrCH}_3(\text{I})(\text{PiPr}_3)]$ were obtained from the dihalide precursors $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrX}_2(\text{PiPr}_3)]$ ($\text{X} = \text{Br}, \text{iodo}$) and CH_3MgI in the molar ratio of 1:2 or 1:1, resp.

RE.CNT 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 2 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 2002:881497 CAPLUS
DN 139:261337
TI Product class 8: four-membered rings with one or more heteroatoms
AU Regitz, M.; Bergstraesser, U.
CS Germany
SO Science of Synthesis (2002), 9, 135-181
 CODEN: SSCYJ9
PB Georg Thieme Verlag
DT Journal; General Review
LA English
AB A review describes the synthesis of various compds. containing four-membered rings with one or more heteroatoms. Covered reactions include ring transformations and ring-closure reactions.

RE.CNT 288 THERE ARE 288 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 3 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 2002:881458 CAPLUS
DN 139:350763
TI Product class 6: organometallic complexes of iridium
AU O'Connor, J. M.
CS Dept. of Chemistry & Biochemistry, University of California - San Diego, La Jolla, CA, 92093-0358, USA
SO Science of Synthesis (2002), 1, 617-744
 CODEN: SSCYJ9
PB Georg Thieme Verlag
DT Journal; General Review
LA English
AB A review on the preparation and applications of iridium organometallic complexes.

RE.CNT 373 THERE ARE 373 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 4 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 2002:444615 CAPLUS
DN 137:279281
TI Formation of planar-chiral alkylphosphine- and aniline-substituted cyclopentadienyl metal complexes and their reactivity toward electrophiles
AU Paisner, Sara N.; Lavoie, Gino G.; Bergman, Robert G.
CS Department of Chemistry and the Center for New Directions in Organic Synthesis (CNDOS), University of California, Berkeley, CA, 94720-1460, USA
SO Inorganica Chimica Acta (2002), 334, 253-275
 CODEN: ICHAA3; ISSN: 0020-1693
PB Elsevier Science B.V.
DT Journal
LA English
OS CASREACT 137:279281
AB A wide range of transition metal complexes containing aniline- and alkylphosphine-substituted cyclopentadienyl ligands have been synthesized: $\text{CpPIr}(\text{CH}_3)_2$ (5), $\text{CpPIr}(\text{H})(\text{Li})$ (11a,b), $\text{CpPIr}(\text{H})(\text{SnPh}_3)$ (13a,b) ($\text{CpP} = 1\text{-}(2\text{-dimethylphosphino-1,1-dimethylethyl})\text{-3-tert-butylcyclopentadienyl}$), $\text{CpNIr}(\text{C}_2\text{H}_4)_2$ (7), CpNIrI_2 (8), $\text{CpNIr}(\text{O}_3\text{SCF}_3)_2$ (9), $\text{CpN}(\text{PMe}_3)\text{IrI}_2$ (10), $\text{CpN}(\text{PMe}_3)\text{IrH}_2$ (2), $\text{CpN}(\text{PMe}_3)\text{Ir}(\text{H})(\text{Li})$ (15a,b), $\text{CpN}(\text{PMe}_3)\text{Ir}(\text{H})(\text{SnPh}_3)$ (16a,b) ($\text{CpN} = 1\text{-}(2\text{-dimethylamino})\text{phenyl-3-tert-butylcyclopentadienyl}$), CpPZrCl_3 (18), $\text{CpPZr}(\text{CH}_2\text{Ph})_3$ (23), $\text{CpPZr}(\text{CH}_2\text{Ph})_2\text{Cl}$ (20), $[(\text{CpP})\text{TiCl}_3]_2$

(22), CpNCp'ZrCl₂ (Cp' = Cp (23), Cp* (24)), and CpPCp'ZrCl₂ (Cp' = Cp (25), Cp* (26)). The presence of the planar-chiral CpP and CpN ligands dramatically changes the reactivity at the metal center in comparison to that of the analogous unchelated and achiral pentamethylcyclopentadienyl (Cp*) complexes. Lithium salts 11 and 15 were obtained by deprotonation of dihydride 2 and the earlier prepared dihydride CpPIrH₂ (1) with tert-butyllithium; these reactive species show diastereoselectivity in their reactions with Ph₃SnCl to form 13a,b and 16a,b, resp. One enantiomer of diiodide 3 was found to react selectively with (R)-binaphthol to form (R,R)-CpPIr(binaphtholate) (17a) leaving (S)-3 unreacted. Attempts to sep. the enantiomers of 3 and 17a were unsuccessful, however, due to the lack of difference in their solubility DFT calcns. carried out on the two possible diastereomers 17a and 17b correctly predict the exclusive formation of 17a. The zirconium and titanium complexes catalyze the polymerization of ethylene to polyethylene and propylene to isotactic polypropylene in the presence of MAO co-catalyst. Compds. 24 and 26 can be methylated to form Cp'Cp*ZrMe₂ (Cp' = CpN (27), CpP (28)).

RE.CNT 58 THERE ARE 58 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 5 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 2001:661433 CAPLUS
DN 135:211151
TI Selective and thermally induced borylation of primary C-H bonds in hydrocarbons catalyzed by iridium and rhodium organometallic complexes
IN Chen, Huiyan; Hartwig, John F.; Semple, Thomas Carl
PA Shell Internationale Research Maatschappij BV, Neth.; Yale University
SO PCT Int. Appl., 66 pp.
CODEN: PIXXD2
DT Patent
LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 2001064689	A1	20010907	WO 2001-EP2407	20010301 <--
	W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW				
	RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
	US 6451937	B1	20020917	US 2000-516897	20000301 <--
	CA 2401695	A1	20010907	CA 2001-2401695	20010301 <--
	EP 1259517	A1	20021127	EP 2001-909815	20010301 <--
	EP 1259517	B1	20030917		
	R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR				
	JP 2003525300	T	20030826	JP 2001-564185	20010301 <--
	AT 250069	T	20031015	AT 2001-909815	20010301 <--
	CN 1524084	A	20040825	CN 2001-807302	20010301
	ZA 2002007214	A	20030717	ZA 2002-7214	20020909 <--
	AU 2004201832	A1	20040520	AU 2004-201832	20040430
PRAI	US 2000-516897	A	20000301		
	WO 2001-EP2407	W	20010301		

OS CASREACT 135:211151

AB A process for selectively functionalizing an aliphatic hydrocarbon and/or alkyl branched alicyclic hydrocarbon at a primary C-H hydrocarbon bond comprising thermally reacting a functionalizing reagent and the hydrocarbon in the presence of a catalyst, said catalyst comprising: (a) a source of a transition metal; (b) a source of a 3 to 8, cyclic or

noncyclic, aromatic or nonarom., neutral, cationic or anionic, substituted or unsubstituted, electron donor moiety which does not dissociate under thermal reaction conditions, wherein said moiety (i) lacks aromatic C-H bonds on the moiety directly bonded to the transition metal, or (ii) contains sterically hindered aromatic C-H bonds on the moiety directly bonded to the transition metal; and (c) a source of ligands capable of formally donating an electron pair to the transition metal of (a) and which dissociate thermally; and wherein said functionalizing reagent comprises a source of boron. For example, in a dry box, a solution containing 0.00125 mmol of the $\text{Cp}^*\text{Rh}(\text{C}_2\text{H}_2)_2$ catalyst and 31.7 mg (0.125 mmol) B2pin2 (B2pin2 = $(\text{OCMe}_2\text{CMe}_2\text{O})\text{BB}(\text{OCMe}_2\text{CMe}_2\text{O})$) in 0.7 mL of dry n-octane was placed in a screw-cap NMR sample tube and sealed tightly. The sample was removed from the box and placed in a 150 °C oil bath. The solution was heated for 80 h at 150 °C and monitored periodically by ^{11}B NMR spectroscopy until HBpin was completely consumed. The sample was brought into the dry box and a solution of dodecahydrotriphenylene (15.2 mg, 0.0632 mmol; reference) in

benzene was added by pipet. An aliquot was then removed and analyzed by GC. The yield of the (1-octyl)Bpin functionalized product was 72%; 100% of the B2pin2 was reacted. The catalyst turnover count was 144. The amount of time taken to convert B2pin2 was 80 min. The selectivity toward the 1-octylBpin product at the primary C-H bond was exclusive, 99.9+%. Other octyl byproducts were not detected. Other catalysts described in examples include: $\text{Cp}^*\text{Ir}(\text{C}_2\text{H}_2)_2$, $\text{Cp}^*\text{Rh}(\text{CH}_2:\text{CHSiMe}_3)_2$, $\text{Cp}^*\text{RhH}_2(\text{SiEt}_3)_2$ and $[(\eta^4\text{-C}_6\text{Me}_6)\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)]$.

RE.CNT 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 6 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1996:156881 CAPLUS
DN 124:261325
TI "Solvent-Free" Photochemical Activation of CH_4 , C_2H_4 , and C_2H_6 by $(\text{C}_5\text{Me}_5)\text{Ir}(\text{CO})_2$ in Supercritical Fluid Solution
AU Banister, James A.; Cooper, Andrew I.; Howdle, Steven M.; Jobling, Margaret; Poliakoff, Martyn
CS Department of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK
SO Organometallics (1996), 15(7), 1804-12
CODEN: ORGND7; ISSN: 0276-7333
PB American Chemical Society
DT Journal
LA English
AB The activation of H_2 and light hydrocarbons (CH_4 , C_2H_4 , and C_2H_6) by $\text{Cp}^*\text{Ir}(\text{CO})_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) in supercrit. fluid solution is described. The reactions have been carried out both in the presence of a supercrit. solvent (scCO_2 , scXe , or scCHF_3) or "solvent-free" in the pure supercrit. hydrocarbon (scCH_4 , scC_2H_4 , or scC_2H_6). This is the first use of scCH_4 as a solvent for photochem. reactions. The presence of H_2 in scC_2H_6 greatly enhances the effectiveness of the C-H activation, but even in the presence of D_2 , $\text{Cp}^*\text{Ir}(\text{CO})(\text{H})\text{Et}$ and not $\text{Cp}^*\text{Ir}(\text{CO})(\text{D})\text{Et}$ is formed. Reaction of $\text{Cp}^*\text{Ir}(\text{CO})_2$ with H_2 occurs efficiently in CHF_3 , but C-H activation of C_2H_6 is almost suppressed in this mixed $\text{scC}_2\text{H}_6/\text{scCHF}_3$ fluid, possibly through H-bonding to the metal center. A technique for recovering the products from milligram-scale reactions is described.

L5 ANSWER 7 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1995:793495 CAPLUS
DN 124:8966
TI Aryldiazenido complexes: structure, fluxionality, and properties of the iridium ethylene aryldiazenido complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{C}_2\text{H}_4)(\text{p-N}_2\text{C}_6\text{H}_4\text{OMe})][\text{BF}_4]$ and a comparison with the analogous nitrosyl complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{C}_2\text{H}_4)(\text{NO})][\text{BF}_4]$
AU Yan, Xiaoqian; Einstein, Frederick W. B.; Sutton, Derek
CS Dep. Chem., Simon Fraser Univ., Burnaby, BC, V5A 1S6, Can.
SO Canadian Journal of Chemistry (1995), 73(7), 939-55

PB National Research Council of Canada
DT Journal
LA English
OS CASREACT 124:8966
AB

[Cp*Ir(C₂H₄)(N₂Ar)][BF₄] (1BF₄; Ar = C₆H₄OMe-p) was synthesized by reacting [ArN₂][BF₄] with Cp*Ir(C₂H₄)₂ at low temperature. An initial electrophilic attack of the incoming diazonium ion at Ir, followed by expulsion of C₂H₄, is postulated to account for the mild reaction conditions that are in sharp contrast to the usual inertness of the bis(ethylene) compound toward ligand substitution. The IR and NMR data for 1BF₄ and its 15N α derivative unambiguously establish that the ArN₂ ligand has the singly bent geometry in this complex in solution. The x-ray crystal structure confirms this for the solid state, and establishes that the plane of the aryldiazenido ligand is approx. perpendicular to the plane defined by the Ir atom and the centers of mass of the Cp* and ethylene ligands. An EHMO anal. of the singly bent aryldiazenido ligand was carried out and satisfactorily accounts for the observed orientation of the ArN₂ ligand. An anal. of the variable-temperature ¹H and ¹³C NMR of 1BF₄ indicates that both restricted rotation of the C₂H₄ ligand and a conformational isomerization of the aryldiazenido ligand are occurring, and $\Delta G_{\text{thermod.270}}$ for the ethylene rotation barrier is estimated at $\leq 51.5 \pm 0.4$ kJ mol⁻¹. This is lower than the barrier of $\Delta G_{\text{thermod.353}} = 68.7 \pm 0.2$ kJ mol⁻¹ determined previously for the analogous nitrosyl complex [Cp*Ir(C₂H₄)(NO)][BF₄] (2BF₄) and probably in these half-sandwich complexes both NO and ArN₂ function as single-faced π -acceptors, and in these circumstances ArN₂ is the better π -acceptor. The ethylene in 1BF₄ is readily displaced by PPh₃ to give [Cp*Ir(PPh₃)(N₂Ar)][BF₄] (3BF₄). This reacts with NaBH₄ to yield Cp*IrH(PPh₃)(N₂Ar) (4) in which the ArN₂ ligand has switched to the doubly bent geometry, on the basis of the 15N α NMR chemical shift data. Attempts to synthesize the corresponding chloro analog 5 resulted in only the chloride salt of the singly bent ArN₂ cation 3. For example, reaction of 3BF₄ with HCl yields the aryldiazenido complex [Cp*IrCl(PPh₃)(NHNAr)][BF₄] (6), but deprotonation of this with Et₃N yields 3Cl, not 5. 1BF₄ crystallized in the space group P2₁/n with a 8.5780(10), b 20.5310(23), c 12.0310(15) Å, β 93.500(10)°, and Z = 4. The structure was refined to R_f = 0.0281 from 2611 observed reflections with I₀ \geq 2.5 σ (I₀) in the range 2 θ = 0-50° (Mo-K α).

L5 ANSWER 8 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1995:314876 CAPLUS

DN 122:160902

TI π -Olefin iridium complexes. XXII. C-H activation of aromatic and aliphatic solvent molecules RH in the reaction of [Cp*IrCl₂]₂ with butadienemagnesium with formation of [Cp*Ir(η ³-C₄H₇)R], and crystal structure of [Cp*Ir(η ³-C₄H₇)C₆H₅]

AU Mueller, Joern; Gaede, Petra Escarpa; Qiao, Ke

CS Institut fuer Anorganische und Analytische Chemie, Technischen Universitaet Berlin, Berlin, D-10623, Germany

SO Zeitschrift fuer Naturforschung, B: Chemical Sciences (1994), 49(12), 1645-53

CODEN: ZNBSEN; ISSN: 0932-0776

PB Verlag der Zeitschrift fuer Naturforschung

DT Journal

LA German

OS CASREACT 122:160902

AB Reactions of [Cp*IrCl₂]₂ (Cp* = η ⁵-C₅Me₅) with [MgC₄H₆.2 THF]_n at low temperature gave [Cp*Ir(η ⁴-C₄H₆)] together with [Cp*Ir(η ³-C₄H₇)R] compds., the latter being formed via C-H activation of solvent mols. RH (RH = benzene, toluene, anisole, thiophene, furan, N-methylpyrrole, pentane, cyclohexane, THF). In the case of pyrrole, C-N-activation occurs. The ratio of syn and anti isomers of the 1-methylallyl complexes

as well as the sites of C-H activation of RH were investigated by NMR spectrometry. An enantiomorphous crystal of $[\text{Cp}^*\text{Ir}(\eta^3\text{-C}_4\text{H}_5)\text{C}_6\text{H}_5]$ was characterized by x-ray diffraction anal. which reveals trigonal planar coordination at the Ir atom and an exo, syn conformation of the 1-methylallyl ligand. A mechanism of the reaction which involves 16-electron intermediates is discussed. The corresponding system $[\text{Cp}^*\text{RhCl}_2]_2/\text{butadienemagnesium}/\text{RH}$ gives only $[\text{Cp}^*\text{Rh}(\eta^4\text{-C}_4\text{H}_6)]$, and no C-H activation is observed

L5 ANSWER 9 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1995:142453 CAPLUS

DN 122:81595

TI Hydrocarbon bridged complexes. XXIX. Nucleophilic addition of carbonylmetallates to cationic allyl- and alkene-complexes of tungsten, manganese, rhenium, iron, ruthenium, osmium, cobalt and iridium: σ, π -allyl and σ, σ -alkene bridged di-, tri-, and tetranuclear complexes

AU Hueffer, Stephan; Wieser, Michael; Polborn, Kurt; Beck, Wolfgang

CS Institut fuer Anorganische Chemie der Ludwig-Maximilians-Universitaet Muenchen, Meiserstrasse 1, Munchen, 80333, Germany

SO Journal of Organometallic Chemistry (1994), 481(1), 45-55
CODEN: JORCAI; ISSN: 0022-328X

PB Elsevier

DT Journal

LA German

OS CASREACT 122:81595

AB The addition of carbonylmetallates $[\text{Lm}(\text{OC})_n\text{M}]$ - to various cationic transition metal complexes with open and cyclic allyl ligands gives heterodi-, tri- and tetrametallic μ - $\eta^1:\eta^2$ -hydrocarbon-bridged complexes in a directed way. The nucleophilic attack always takes place on a terminal carbon atom of the allyl group. The same regioselectivity was observed with $[\text{Cp}^*\text{Ir}(\eta^2\text{-C}_2\text{H}_4)(\eta^3\text{-C}_3\text{H}_5)]^+$ and $[(\text{OC})_3\text{Fe}(\eta^2:\eta^3\text{-1,2,3-bicyclooctadienyl})]^+$. The structure of $\text{Cp}^*\text{Ir}(\eta^2\text{-C}_2\text{H}_4)(\mu\text{-}\eta^1:\eta^2\text{-C}_3\text{H}_5)\text{Re}(\text{CO})_5$ was determined by x-ray diffraction. Only with $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta^2:\eta^3\text{-C}_8\text{H}_{11})]^+$ the attack of $[\text{Re}(\text{CO})_5]^-$ occurs on the alkene function of the cyclooctadienyl ligand.

L5 ANSWER 10 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1994:605639 CAPLUS

DN 121:205639

TI Rhodium and Iridium Complexes with the 1-(2-(Dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl Ligand

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SO Organometallics (1994), 13(10), 3854-61

CODEN: ORGND7; ISSN: 0276-7333

DT Journal

LA English

OS CASREACT 121:205639

AB Some new Rh(I), Rh(III), Ir(I), and Ir(III) complexes containing the 1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl (Cp^1) ligand are described. The bis(ethene) complexes $\text{Cp}^1\text{Rh}(\text{C}_2\text{H}_4)_2$ (2), and $\text{Cp}^1\text{Ir}(\text{C}_2\text{H}_4)_2$ (3) with a noncoordinating dimethylamino function are synthesized by reaction of $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ with Cp^1Li and by the reaction of $[(\text{COE})\text{IrCl}]_2$ with $\text{Cp}^1\text{Li}/\text{C}_2\text{H}_4$, resp. Addition of iodine to 2 or 3 results in the formation of the resp. diiodo complexes Cp^1RhI_2 (4) and Cp^1IrI_2 (5) with intramol. amino coordination. In the presence of CO, 4 or 5 can easily be transferred into the carbonyl complexes $\text{Cp}^1\text{RhI}_2(\text{CO})$ (6) and $\text{Cp}^1\text{IrI}_2(\text{CO})$ (7), resp., with a noncoordinating amino function. The reverse reaction is successful for both 6 and 7, but under differing conditions. In the reaction of 4 and 5 with PMe_3 , PPh_3 , and CNCMe_3 , the corresponding substitution products $\text{Cp}^1\text{MI}_2\text{L}$ (8-12) are formed. Reduction of 4 and 5 with Na-Hg under a CO atmosphere leads to the carbonyl complexes $\text{Cp}^1\text{Rh}(\text{CO})_2$ (13) and $\text{Cp}^1\text{Ir}(\text{CO})_2$ (14), resp., with a noncoordinating amino

group. In the reaction of 4 and 5 with Ag₂C₂O₄, the oxalato complexes Cp₁RhC₂O₄ (15) and Cp₁Ir(C₂O₄) (16), resp., are formed. The coordinating amino group in 15 and 16 can be replaced by the PMe₃ ligands to give Cp₁(Me₃P)Rh(C₂O₄) (17) and Cp₁Ir(PMe₃)(C₂O₄) (18). The crystal structures of 4 and 5 were determined

L5 ANSWER 11 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1994:604749 CAPLUS

DN 121:204749

TI Design and Study of Rh(III) Catalysts for the Selective Tail-to-Tail Dimerization of Methyl Acrylate

AU Hauptman, Elisabeth; Sabo-Etienne, Sylviane; White, Peter S.; Brookhart, Maurice; Garner, J. Michael; Fagan, Paul J.; Calabrese, Joseph C.

CS Department of Chemistry, University of North Carolina, Chapel Hill, NC, 27599-3290, USA

SO Journal of the American Chemical Society (1994), 116(18), 8038-60

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

OS CASREACT 121:204749

AB The development of an efficient, highly selective Rh(III) catalyst system for the tail-to-tail dimerization of Me acrylate (MA) to di-Me hexenedioates, precursors to adipic acid, is described. The catalytic cycle is entered by protonation of Cp^{*}Rh(C₂H₄)₂ (Cp^{*} = C₅Me₅) to yield Cp^{*}Rh(C₂H₄)(CH₂CH₂-μ-H)⁺ (7) followed by reaction with Me acrylate. The catalyst resting state has been generated by low-temperature protonation of Cp^{*}Rh(CH₂CHCO₂CH₃)₂ (15) and identified as Cp^{*}Rh(CH₂CH₂COOMe)(η²-CH₂CHCO₂Me)⁺ (8) by ¹H and ¹³C NMR spectroscopy. Investigation of iridium analogs has led to the isolation and X-ray structural characterization of Cp^{*}Ir(CH₂CH₂COOMe)(η²-CH₂CHCO₂Me)⁺ (23a), in which the orientation of the acrylate ligands is that required for tail-to-tail coupling. At -23°, complex 8 undergoes β-migratory insertion to give Cp^{*}RhCH(CH₂COOMe)(CH₂CH₂COOMe)⁺ (10). Complex 10 was independently synthesized by treatment of complex 7 with trans-MeO₂CCH:CHCH₂CH₂CO₂Me and was characterized by X-ray crystallog. The free energy of activation for the migration reaction is 18.7 kcal/mol and matches that based on the catalytic turnover (TO) frequency (6.6 TO/min at 25 °C, ΔG_{thermod.} = 19 kcal/mol). This observation confirms 8 as the resting state and the C-C coupling reaction as the turnover-limiting step. The catalyst deactivates by formal loss of H₂ from complex 10 to produce Cp^{*}Rh(η³-CH₃OCOCH₂CHCHCHCO₂CH₃)⁺ (9). The structure of complex 9 was verified by an X-ray crystallog. study. Exposure of 9 to an atmospheric of H₂

in

the presence of MA regenerates the resting state 8, and dimerization proceeds. Second generation catalysts with increased activity and lifetimes have been developed by replacing the C₅Me₅ ligand by methylated indenyl ligands. Using the catalytic system derived from (1,2,3-trimethylindenyl)Rh(C₂H₄)₂ (11), conversion of 54,000 equiv of Me acrylate to di-Me hexenedioates could be achieved after 68 h at 55 °C under N₂. Details of the mechanism have been elucidated and resemble closely those of the Cp^{*} system. Similar intermediates to 8 and 10 have been characterized by ¹H and ¹³C NMR spectroscopy. In contrast, treatment with Me acrylate of the more electrophilic systems derived from CpRh(C₂H₄)₂ (25) (Cp = C₅H₅) and Cp_{thermod.}Rh(C₂H₄)₂ (30) [Cp_{thermod.} = C₅(CH₃)₄CF₃] results in slow dimerization. Low-temperature protonation of CpRh(CH₂CHCO₂CH₃)₂ (27) with H(Et₂O)₂Bar'⁴ yields a mixture of rhodium species which upon warming to 23°C converge to the bis-chelate complex CpRhCH(CH₂COOMe)(CH₂CH₂COOMe)⁺ (28). Exposure of complex 28 to MA generates the unusual bridged species CpRh(CH₂CHCOOCH₃)H(CH₂CHCOOCH₃)⁺ (29), which serves as the resting state during dimerization. Treatment of complex 30 with H(Et₂O)₂Bar'⁴ yields Cp_{thermod.}Rh(C₂H₄)(CH₂CH₂-μ-H)⁺ (31), which upon reaction with MA clearly produces Cp_{thermod.}RhCH(CH₂COOMe)(CH₂CH₂COOMe)⁺ (33), and dimerization proceeds.

Finally, attempts to catalyze the dimerization of other functionalized olefins including Me vinyl ketone, Me crotonate, 2-vinylpyridine, and 1-vinyl-2-pyrrolidinone are presented.

L5 ANSWER 12 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1994:435824 CAPLUS
DN 121:35824
TI (Pentamethylcyclopentadienyl)nitrosyl(ethylene)iridium Tetrafluoroborate, [(η^5 -C5Me5)Ir(NO)(C2H4)][BF4]: Synthesis, Characterization, and Some Reactions. X-ray Crystal Structures of the Title Compound and Its Derivatives (η^5 -C5Me5)Ir(NO)(CH2CH2OEt) and (η^5 -C5Me5)2Ir2X2(μ -X)(μ -NO) (X = Br, I)
AU Batchelor, Raymond J.; Einstein, Frederick W. B.; Lowe, Nigel D.; Palm, Bradley A.; Yan, Xiaoqian; Sutton, Derek
CS Department of Chemistry, Simon Fraser University, Burnaby, BC, V5A 1S6, Can.
SO Organometallics (1994), 13(5), 2041-52
CODEN: ORGND7; ISSN: 0276-7333
DT Journal
LA English
OS CASREACT 121:35824
AB [(η^5 -C5Me5)Ir(NO)(C2H4)][BF4] (1) was prepared by the reaction of (η^5 -C5Me5)Ir(C2H4)2 with [NO][BF4] in acetone at -10°. The crystal structure of 1 was determined. The Ir-NO group is linear, with N-O = 1.15(1) Å, Ir-N = 1.762(9) Å, and Ir-N-O = 175.8(9)°; the IR spectrum in ethanol exhibits ν (NO) = 1821 cm⁻¹, confirmed by 15N enrichment [ν (15NO) = 1786 cm⁻¹]. The ethylene ligand is sym. bound to iridium with bond lengths Ir-C(1) = 2.19(1) Å, Ir-C(2) = 2.17(1) Å, and C(1)-C(2) = 1.37(2) Å and is oriented with the C(1)-C(2) axis approx. perpendicular to the plane defined by N and the centers of mass of the η^5 -C5Me5 and η^2 -C2H4 ligands, resp. The barrier to ethylene rotation was determined from variable-temperature 1H NMR data at the coalescence temperature (Tc = 353 K). Products of reaction of 1 with KI, KBr, KCl, NaOEt, and (η^5 -C5Me5)Ir(CO)2 are described. Reaction with KI in ethanol at room temperature gives (η^5 -C5Me5)Ir(NO)I and at 60° gives the binuclear compound (η^5 -C5Me5)2Ir2I2(μ -I)(μ -NO) (2). (η^5 -C5Me5)Ir(NO)I has ν (NO) = 1761 cm⁻¹ [ν (15NO) = 1717 cm⁻¹] in CDCl3 indicating a terminal linear nitrosyl group. The crystal structure of 2·toluene was determined. Complex 2 has mutually trans η^5 -C5Me5 groups, trans terminal iodide ligands, and sym. bridging nitrosyl and iodide with Ir(1)-N = 2.029(12) Å, Ir(2)-N = 1.974(12) Å, and N-O = 1.24(2) Å. The reaction of 1 with KBr in ethanol at room temperature produces (η^5 -C5Me5)Ir(NO)Br in solution but this converts on attempted isolation to other products which include (η^5 -C5Me5)Ir2Br2(μ -Br)(μ -NO) (3). The structure of 3 is essentially similar to that of 2, but is disordered about a crystallog. inversion center. In contrast to these ethylene displacement reactions, NaOEt reacts with 1 to produce the ethoxyethyl derivative (η^5 -C5Me5)Ir(NO)(CH2CH2OEt) (4), the crystal structure of which was also determined. The reaction of 1 with (η^5 -C5Me5)Ir(CO)2 in refluxing ethanol yielded [(η^5 -C5Me5)2Ir2(μ -CO)(μ -NO)][BF4], identified on the basis of anal. and spectroscopic data.

L5 ANSWER 13 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1994:322409 CAPLUS
DN 120:322409
TI Rh(III) catalysts for tail-to-tail dimerization of methyl acrylate
AU Brookhart, Maurice; Hauptman, Elisabeth; Sabo-Etienne, Sylviane
CS Dep. Chem., Univ. North Carolina Chapel Hill, North Carolina, 27599-3290, USA
SO Org. Synth. Organomet. (OSM4), Proc. Symp., 4th (1993), Meeting Date 1992, 69-77. Editor(s): Enders, Dieter; Gais, Hans-Joachim; Keim, Wilhelm. Publisher: Vieweg, Wiesbaden, Germany.
CODEN: 59SKAA

DT Conference
LA English
AB A conference in which Cp* is Me₅C₅. The development of an efficient, highly selective Rh(III) catalyst system for the tail-to-tail dimerization of Me acrylate is described. The catalytic cycle is entered by protonation of Cp*Rh(C₂H₄)₂ to yield Cp*(C₂H₄)RhCH₂CH₂-μ-H⁺, followed by reaction with Me acrylate. The catalyst resting state has been generated by low-temperature protonation of Cp*Rh(CH₂CHCO₂Me)₂ and identified. The turnover-limiting step is the C-C coupling reaction from the resting state. Addnl. low temperature NMR expts. provide a complete picture of the catalytic cycle. Investigation of Ir analogs has led to the isolation and X-ray structural characterization of a complex thought to be isostructural with the Rh resting state.

L5 ANSWER 14 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1993:259466 CAPLUS

DN 118:259466

TI Low-temperature chemical vapor deposition or laser photodeposition of metals on substrates by using organometallic compounds

IN Hicks, Robert F.; Kaesz, Herbert D.; Xu, Dagiang

PA University of California, Berkeley, USA

SO U.S., 8 pp. Cont.-in-part of U.S. Ser. No. 260,799, abandoned.

CODEN: USXXAM

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	US 5130172	A	19920714	US 1989-428245	19891026 <--
PRAI	US 1988-260799	B2	19881021		

AB Metals are deposited on Si or W substrates at .apprx.20-≤190° by using organometallic compound LnMR_m in presence of H. L in the compound is H, ethylene, allyl, methylallyl, butadienyl, pentadienyl, cyclopentadienyl, methylcyclopentadienyl, cyclohexadienyl, hexadienyl, cycloheptatrienyl, or a derivative of these compds. having ≥1 C₅ alkyl side chain; M is a metal that can readily cycle between 2 oxidation states and can catalyze hydrogenation of hydrocarbon ligands of the compound; R is Me, Et, Pr, or Bu; and n and m are each a number from 0 to the valence of the metal. The compound is vaporized at .apprx.20-100°. M is selected from the group of metals having atomic number 22-29, 40-47, and 72-79 or 25-29, 42-47, and 74-79 or Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, and W.

L5 ANSWER 15 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1993:213268 CAPLUS

DN 118:213268

TI Synthesis and isolation of highly reactive η³-allyl alkyne complexes of iridium via the inner-sphere η³-allyl triflate complex (C₅Me₅)Ir(η³-C₃H₅)OTf. Facile conversion to alkyne metallacyclobutane complexes by nucleophilic addition

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SO Organometallics (1993), 12(3), 600-2

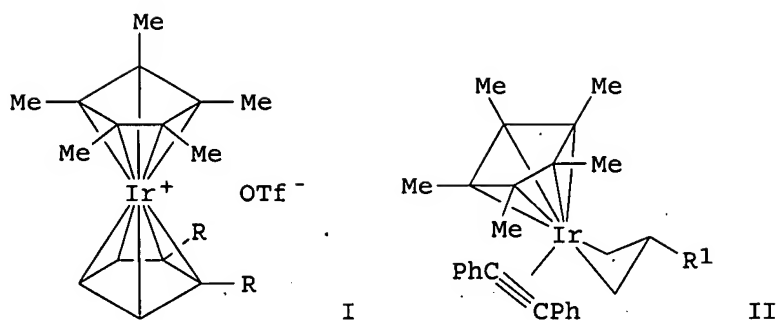
CODEN: ORGND7; ISSN: 0276-7333

DT Journal

LA English

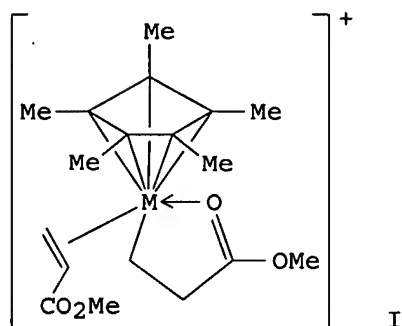
OS CASREACT 118:213268

GI



AB The inner-sphere triflate complex $[(C_5Me_5)Ir(\eta^3-C_3H_5)OTf]$, formed quant. on photolysis of $[(C_5Me_5)Ir(\eta^3-C_3H_5)(\eta^2-C_3H_6)]+OTf^-$, reacts with disubstituted alkynes to form the isolable, but highly reactive, allyl alkyne complexes $[(C_5Me_5)Ir(\eta^3-C_3H_5)(RC.tplbond.CR)]+OTf^-$ ($R = Me, Ph$), inaccessible by conventional methodol. Although the allyl alkyne complexes undergo facile reductive ligand coupling to form the substituted bis(cyclopentadienyl) complexes I, these complexes can be isolated and converted selectively to the metallacyclobutane alkyne complexes II ($R_1 = H, Me, CN, MeCHBz$) in high yield by reaction with nucleophiles.

L5 ANSWER 16 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
 AN 1992:408168 CAPLUS
 DN 117:8168
 TI Mechanism of rhodium(III)-catalyzed methyl acrylate dimerization
 AU Brookhart, Maurice; Hauptman, Elisabeth
 CS Dep. Chem., Univ. North Carolina, Chapel Hill, NC, 27599-3290, USA
 SO Journal of the American Chemical Society (1992), 114(11), 4437-9
 CODEN: JACSAT; ISSN: 0002-7863
 DT Journal
 LA English
 OS CASREACT 117:8168
 GI



AB Protonation of $Cp^*Rh(C_2H_4)_2$ ($Cp^* = \eta^5$ -pentamethylcyclopentadienyl) in the presence of Me acrylate generates a highly efficient catalytic system for the selective tail-to-tail dimerization of Me acrylate. Mechanistic details of this cycle have been elucidated. The catalyst resting state was generated by protonation of $Cp^*Rh(CH_2:CHCO_2Me)_2$ at -78° and identified by 1H and ^{13}C NMR spectroscopy as complex I ($M = Rh$). The analogous I ($M = Ir$) was synthesized; x-ray anal. of which strongly suggests, by comparison, a structure of I ($M = Rh$) in which the orientation of the acrylate ligands is that required for tail-to-tail coupling. At -23° I ($M = Rh$) undergoes β -migratory insertion to give $Cp^*RhCH(CH_2CO_2Me)(CH_2CH_2CO_2Me)^+$ (II). The free energy of

activation for this process is 18.7 kcal/mol and matches that based on the catalytic turnover frequency. This observation confirms I (M = Rh) as the resting state and the C:C coupling reaction as the turnover-limiting step. Treatment of II with Me acrylate results in rapid displacement of dimer to regenerate species I (M = Rh) and thereby closes the catalytic cycle.

L5 ANSWER 17 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1992:235830 CAPLUS

DN 116:235830

TI Sequential displacement of coordinated ethene by hexafluorobenzene: crystal structures of η^2 - and η^4 -hexafluorobenzene complexes of iridium

AU Bell, Tanachai W.; Helliwell, Madeleine; Partridge, Martin G.; Perutz, Robin N.

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SO Organometallics (1992), 11(5), 1911-18

CODEN: ORGND7; ISSN: 0276-7333

DT Journal

LA English

AB The photochem. reaction of $(\eta^5\text{-C}_5\text{R}_5)\text{Ir}(\text{C}_2\text{H}_4)_2$ (R = H, Me) with hexafluorobenzene effects sequential replacement of coordinated ethene by hexafluorobenzene, yielding $(\eta^5\text{-C}_5\text{R}_5)\text{Ir}(\text{C}_2\text{H}_4)(\eta^2\text{-C}_6\text{F}_6)$ (I) followed by $(\eta^5\text{-C}_5\text{R}_5)\text{Ir}(\eta^4\text{-C}_6\text{F}_6)$ (II). I is present in solution as two isomers which interconvert slowly compared with the NMR relaxation time, T_1 . The dominant isomer of I exhibits coupling between ethene nuclei and ^{19}F , suggestive of a C-H...F interaction. The minor isomer is postulated to be related to the major isomer by 180° rotation about the vector joining Ir to the midpoint of the coordinated C-C bond of C_6F_6 . All the complexes exhibit three mutually coupled resonances in the ^{19}F NMR spectrum, indicating that the C_6F_6 units are stereochem. rigid. The x-ray crystal structure of I and II (R = H) were determined

L5 ANSWER 18 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1991:559400 CAPLUS

DN 115:159400

TI Metallacyclobutanes from kinetic nucleophilic addition to η^3 -allyl ethylene complexes of iridium. Regioselectivity dependence on nucleophile and allyl orientation

AU Wakefield, James B.; Stryker, Jeffrey M.

CS Dep. Chem., Indiana Univ., Bloomington, IN, 47405, USA

SO Journal of the American Chemical Society (1991), 113(18), 7057-9

CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

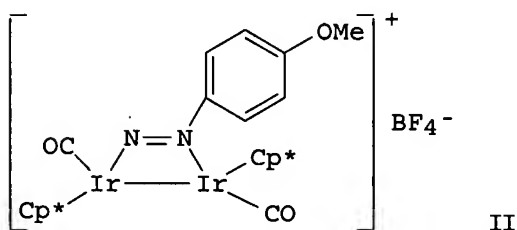
AB The addition of nucleophiles to both endo- and exo-isomers of the η^3 -allyl ethylene complex $(\text{C}_5\text{Me}_5)\text{Ir}(\eta^2\text{-C}_2\text{H}_4)(\eta^3\text{-C}_3\text{H}_5)^+ \text{OTf}^-$ has been investigated. Contrary to predictions based on the selectivity rules of Davies, Green, and Mingos (1978) kinetic nucleophiles such as hydride and organic enolates react regioselectively at the η^3 -allyl central C, giving metallacyclobutane complexes. With the enolate of propiophenone, the two η^3 -allyl stereoisomers return metallacyclobutane products isomeric at the β -carbon, indicating that the nucleophile does not induce endo-exo isomerization prior to addition. Iodolysis of the metallacyclobutanes at low temperature releases the organic

as

the substituted cyclopropane and returns the metal as $[(\text{C}_5\text{Me}_5)\text{IrI}_2]_2$, which can be converted back to the starting allyl ethylene complex in a single step. The reaction of weaker nucleophiles, such as potassium dimethylmalonate, does not lead to metallacyclobutane formation. Instead, these reactions reveal an unexpected regioselectivity dependence on the configuration of the allyl ligand: the exo-allyl complex returns exclusively an ethylene adduct, while the endo-allyl complex suffers addition to the terminal carbon of the allyl ligand. These results demonstrate a

considerably more complex reactivity profile than expected.

L5 ANSWER 19 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1991:82070 CAPLUS
DN 114:82070
TI A dinuclear iridium aryldiazenide complex with a μ^2 - η^2 -N,N' bridge.
Synthesis of $[(C_5Me_5)_2Ir_2(CO)_2(\mu^2-\eta^2-NNC_6H_4OMe)][BF_4]$ from
 $[(C_5Me_5)Ir(C_2H_4)(N_2C_6H_4OMe)][BF_4]$
AU Einstein, Frederick W. B.; Yan, Xiaoqian; Sutton, Derek
CS Dep. Chem., Simon Fraser Univ., Burnaby, BC, V5A 1S6, Can.
SO Journal of the Chemical Society, Chemical Communications (1990),
(21), 1466-7
CODEN: JCCCCAT; ISSN: 0022-4936
DT Journal
LA English
OS CASREACT 114:82070
GI



AB $[(C_5Me_5)Ir(C_2H_4)(p-N_2C_6H_4OMe)][BF_4]$ (I) and the nitrosyl analog $[(C_5Me_5)Ir(C_2H_4)(NO)][BF_4]$, have been synthesized from $(C_5Me_5)Ir(C_2H_4)_2$ and $[p-N_2C_6H_4OMe][BF_4]$ or $[NO][BF_4]$; I reacts with $(C_5Me_5)Ir(CO)_2$ to give the title dinuclear complex II (Cp^* = pentamethylcyclopentadienyl) in which the aryldiazenide ligand bridges in the four-membered dimetalladiaza-ring fashion.

L5 ANSWER 20 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1990:515544 CAPLUS
DN 113:115544
TI Ethylene-assisted allylic carbon-hydrogen bond activation of substituted alkenes using dicationic iridium complexes. Synthesis, structure, and configurational isomerism of cationic iridium η^3 -allyl ethylene complexes
AU Wakefield, James B.; Stryker, Jeffrey M.
CS Dep. Chem., Indiana Univ., Bloomington, IN, 47405, USA
SO Organometallics (1990), 9(9), 2428-30
CODEN: ORGND7; ISSN: 0276-7333
DT Journal
LA English
OS CASREACT 113:115544
AB The use of ethylene as a sterically small, chemical inert, enabling ligand allows the dicationic iridium tris(solvate) complex $[Cp^*Ir(S)_3]^{2+} (OTf^-)_2$ (OTf^-)₂ (S = acetone, Cp^* = η^5 -C₅Me₅, OTf^- = triflate) to mediate allylic carbon-hydrogen bond activation of substituted olefins, giving monocationic η^3 -allyl complexes of the form $[Cp^*(C_2H_4)(\eta^3\text{-allyl})]^+ OTf^-$, where the allyl is mono- or disubstituted, in high yield. In the absence of ethylene, the reaction fails for simple olefins larger than propene itself. This allylic activation selectively provides the thermodynamically less stable exo isomer of the allyl ligand. In the parent allyl ethylene complex, isomerization to the thermodyn. endo isomer is observed on treatment with triphenylphosphine; no substitution of the ethylene ligand is observed. Photolysis of the thermodyn. endo isomer returns the kinetic exo isomer. In contrast, the substituted crotyl ethylene

complex on treatment with triphenylphosphine leads to clean substitution of the thylene, providing $[\text{Cp}^*(\text{Ph}_3\text{P})\text{Ir}(\text{crotyl})]^+ \text{OTf}^-$. Isomerization of the kinetic exo isomer in the crotyl complex is obtained thermally in the absence of added ligand; quant. conversion is obtained by heating under ethylene to suppress decomposition by loss of the coordinated ethylene. Both the thermodyn. and endo allyl complex $[\text{Cp}^*\text{Ir}(\text{C}_2\text{H}_4)(\eta^3\text{-allyl})]^+ \text{OTf}^-$ and the kinetic exo crotyl complex $[\text{Cp}^*\text{Ir}(\text{C}_2\text{H}_4)(\eta^3\text{-crotyl})]^+ \text{OTf}^-$ have been characterized by x-ray crystallog. The reaction of 2-pentene with the dication leads to a mixture of isomeric terminal and internal η^3 -allyl complexes, with good selectivity for internal allylic activation.

L5 ANSWER 21 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1988:493287 CAPLUS

DN 109:93287

TI The formation and characterization of $(\eta^2\text{-ethene})\text{hydrido}(\eta^5\text{-pentamethylcyclopentadienyl})$ (trisubstituted-silyl)rhodium complexes; intermediates in catalytic dehydrogenative silylation reactions

AU Ruiz, Jose; Bentz, Peter O.; Mann, Brian E.; Spencer, Catriona M.; Taylor, Brian F.; Maitlis, Peter M.

CS Dep. Chem., Univ. Sheffield, Sheffield, S3 7HF, UK

SO Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999) (1987), (11), 2709-13

CODEN: JCDTBI; ISSN: 0300-9246

DT Journal

LA English

OS CASREACT 109:93287

AB The complexes $[\text{Cp}^*\text{Rh}(\text{H})(\text{SiR}_3)(\text{C}_2\text{H}_4)]$ (I; $\text{Cp}^* = \text{C}_5\text{Me}_5$; $\text{C}_5\text{H}_5 = \eta^5\text{-cyclopentadienyl}$; $\text{R} = \text{Et}, \text{Me}$) were detected and characterized spectroscopically (including 103Rh NMR spectra) as intermediates in the thermal and photochem. reaction, $\text{C}_2\text{H}_4 + [\text{Cp}^*\text{Rh}(\text{H})_2(\text{SiR}_3)_2]$ (II) $\xrightarrow{\text{dblharw.}}$ $[\text{Cp}^*\text{Rh}(\text{C}_2\text{H}_4)_2]$ (III) + R_3SiH . Complex I ($\text{R} = \text{OEt}$), which was isolated and fully characterized, and I ($\text{R} = \text{Ph}$), were obtained from reaction of R_3SiH and $[\text{Cp}^*\text{Rh}(\text{C}_2\text{H}_4)_2]$. Evidence for Ir analogs of I was observed, but reactions were more complex. I were reasonably thermally stable; since II and III are active catalysts for the reaction, $\text{Et}_3\text{SiH} + \text{C}_2\text{H}_4 \rightarrow \text{CH}_2\text{:CHSiEt}_3 + \text{SiEt}_4$, this implies significant activation is required to reorganize the ligands in I. The related reaction of R_3SiH ($\text{R} = \text{Me}, \text{Et}, \text{Ph}, \text{OEt}$) and $[\text{Cp}^*\text{Rh}(\text{CO})_2]$ gave $[\text{Cp}^*\text{Rh}(\text{CO})\text{H}(\text{SiR}_3)]$, which lost R_3SiH to give blue $[[\text{Cp}^*\text{Rh}(\text{CO})]_2]$.

L5 ANSWER 22 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1988:168123 CAPLUS

DN 108:168123

TI Catalytic synthesis of olefins from paraffins in the presence of alkenes and catalyst manufacture

IN Walker, Howard Walter

PA Ethyl Corp., USA

SO Eur. Pat. Appl., 8 pp.

CODEN: EPXXDW

DT Patent

LA English

FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 245061	A1	19871111	EP 1987-303970	19870501 <--
	EP 245061	B1	19891123		
	R: AT, BE, CH, DE, FR, GB, IT, LI, LU, NL, SE				
	US 4670621	A	19870602	US 1986-859696	19860505 <--
	US 4751344	A	19880614	US 1987-37231	19870416 <--
	AT 48128	T	19891215	AT 1987-303970	19870501 <--
PRAI	US 1986-859696	A	19860505		
	US 1987-37231	A	19870416		
	EP 1987-303970	A	19870501		

AB The photochem. or thermal dehydrogenation of saturated hydrocarbons uses catalytic transition metal complexes $RMLnH_m$ ($R = Cp$ or arene which donates 6 electrons; $M =$ transition metal of atomic number 43, 44, 45, 75, 76, or 77; $L =$ alkene or cycloalkene, diene or cyclooctadiene, or triene on cyclooctatriene; $n = 1, 2$, or 3; $M = 0$ or 1) and free alkene hydrogen acceptors. Dehydrogenation of 59 mmol cyclooctane at 225° for 16 h under 300 psig in the presence of C_2H_4 and 52 μ mol bis(ethylene)pentamethylcyclopentadienyl iridium gave 0.54% cyclooctene.

L5 ANSWER 23 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1987:617821 CAPLUS

DN 107:217821

TI The synthesis and characterization of dihydridobis(trialkylstannyl) (pentamethylcyclopentadienyl)rhodium(V) and -iridium(V) complexes and related reactions

AU Ruiz, Jose; Spencer, Catriona M.; Mann, Brian E.; Taylor, Brian F.; Maitlis, Peter M.

CS Dep. Chem., Univ. Sheffield, Sheffield, S3 7HF, UK

SO Journal of Organometallic Chemistry (1987), 325(1-2), 253-60

CODEN: JORCAI; ISSN: 0022-328X

DT Journal

LA English

OS CASREACT 107:217821

AB The complexes $[C_5Me_5M(H)_2(SnR_3)_2]$ ($M = Rh, Ir$; $R = Bu, Me$) were prepd. by reaction of R_3SnH and $[(C_5Me_5M)_2Cl_4]$ or $[C_5Me_5M(C_2H_4)_2]$. An intermediate in the last reaction was spectroscopically identified as $[C_5Me_5M(H)(SnR_3)(C_2H_4)]$ ($M = Ir, R = Me$), but the Rh analog could not be detected. The hydrido carbonyl complexes, $[C_5Me_5M(H)(SnR_3)(CO)]$ (same M, R) were readily obtained by reaction of R_3SnH with $[C_5Me_5M(CO)_2]$; they were more stable than their silyl analogs, but the Rh complexes slowly decomposed. I were very resistant to attack by nucleophiles, but I ($M = Rh, R = Me$) slowly reacted with PPh_3 to give $[C_5Me_5Rh(PPh_3)(SnR_3)_2]$; this behavior was in marked contrast to that shown by $[C_5Me_5Rh(H)_2(SiR_3)_2]$. The complex $[C_5Me_5Rh(H)_2(SnMe_3)_2]$ was deprotonated by $BuLi$ to give $[C_5Me_5Rh(H)(SnMe_3)_2]^-$; this was reversed on addition of $MeOH$.

L5 ANSWER 24 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1987:536327 CAPLUS

DN 107:136327

TI Photochemical catalytic manufacture of alkenes from paraffins

IN Walker, Howard W.

PA Ethyl Corp., USA

SO U.S., 5 pp.

CODEN: USXXAM

DT Patent

LA English

FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 4670621	A	19870602	US 1986-859696	19860505 <--
	US 4751344	A	19880614	US 1987-37231	19870416 <--
	CA 1277997	C	19901218	CA 1987-535816	19870428 <--
	EP 245061	A1	19871111	EP 1987-303970	19870501 <--
	EP 245061	B1	19891123		
	R: AT, BE, CH, DE, FR, GB, IT, LI, LU, NL, SE				
	JP 63022034	A	19880129	JP 1987-108736	19870501 <--
	JP 04040332	B	19920702		
	AT 48128	T	19891215	AT 1987-303970	19870501 <--
PRAI	US 1986-859696	A2	19860505		
	US 1987-37231	A	19870416		
	EP 1987-303970	A	19870501		

OS CASREACT 107:136327

AB The title process comprises transferring H from a saturated hydrocarbon to an alkene via a bis(alkene)cyclopentadienyl Ir mol. complex catalyst in the

presence of free alkene. The reaction may be performed photochem. under UV irradiation or thermolytically with the application of heat. By use of these catalysts it is now routinely possible to use alkenes in general as H acceptors, and while C₂H₄ is the preferred alkene, other alkenes may successfully be employed. Thus, 30 mg bis(ethylene)pentamethylcyclopentadienyl Ir and 2.83 g decane (pretreated with H₂SO₄, passed through silica gel and distilled under N) were charged into an autoclave, the apparatus pressured to 150 psi with C₂H₄, shaken, and the pressure released. The autoclave was then pressurized with C₂H₄ to 150 psi and operated at 246°/340 psi for 19 h, and gas chromatog. anal. of the reaction mixture indicated the presence of C₂H₆ and 16% decenes having the isomer distribution 1-decene 9.58, 2-decene 29.17, 3-decene 30.25, and 4- and 5-decenes 31.22%.

- L5 ANSWER 25 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
 AN 1986:609169 CAPLUS
 DN 105:209169
 TI First example of cyclodimerization of a phosphaaalkyne to a 1,3-diphosphacyclobutadiene. Syntheses of complexes of the type [M(η⁵-C₅R₅){η⁴-Me₃CCP₂}] (R = H or Me; M = Co, Rh, or Ir): crystal and molecular structure of η⁵-pentamethylcyclopentadienyl-2,4-di-tert-butyl-1,3-diphosphacyclobutadienecobalt(I), [Co(η⁵-C₅Me₅){η⁴-(Me₃CCP₂)₂}]
 AU Hitchcock, Peter B.; Maah, Mohd Jamil; Nixon, John F.
 CS Sch. Chem. Mol. Sci., Univ. Sussex, Brighton, BN1 9QJ, UK
 SO Journal of the Chemical Society, Chemical Communications (1986), (10), 737-8
 CODEN: JCCCAT; ISSN: 0022-4936
 DT Journal
 LA English
 OS CASREACT 105:209169
 GI For diagram(s), see printed CA Issue.
 AB Reaction of the bisethylene complexes I (R = H, M = Co, Rh; R = Me, M = Co, Rh, Ir) with Me₃CC.tplbond.P in PhMe at room temperature gave 15-95% yield of the corresponding complexes II, containing the novel 2,4-di-tert-butyl-1,3-diphosphacyclobutadiene ring. The structures of II were determined by spectral methods and confirmed by x-ray crystallog. anal. of II (R = Me, M = Co).
- L5 ANSWER 26 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
 AN 1983:179617 CAPLUS
 DN 98:179617
 TI Approaches to ethyl(pentamethylcyclopentadienyl)rhodium or -iridium complexes
 AU De Miguel, Amelio Vazquez; Maitlis, Peter M.
 CS Dep. Chem., Univ. Sheffield, Sheffield, S3 7HF, UK
 SO Journal of Organometallic Chemistry (1983), 244(2), C35-C37
 CODEN: JORCAI; ISSN: 0022-328X
 DT Journal
 LA English
 AB Reaction of [(C₅Me₅M)₂Cl₄] (M = Rh or Ir) with Al₂Et₆ gives [C₅Me₅M(C₂H₄)₂] and some [C₅Me₅MCl(η³-CH₂CHCHMe)] but [C₅Me₅RhEt₂(PMe₃)] is obtained from the reaction of [C₅Me₅RhCl₂(PMe₃)] with Al₂Et₆.
- L5 ANSWER 27 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
 AN 1979:137976 CAPLUS
 DN 90:137976
 TI Pentamethylcyclopentadienylrhodium and -iridium complexes. Part 18. The reactions of [M(C₅Me₅)(sol)₃][PF₆]₂ (M = Rh or Ir; sol = MeCN, Me₂CO, or MeOH) with mono-, di-, and triolefins
 AU White, Colin; Thompson, Stephen J.; Maitlis, Peter M.
 CS Dep. Chem., Univ. Sheffield, Sheffield, UK
 SO Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999) (1978), (10), 1305-11

DT Journal
 LA English
 AB [ML(MeCN)₃][PF₆]₂ (M = Rh, Ir; L = pentamethylcyclopentadienyl) or [MLCl₂]₂ reacted with bicyclo[2.2.1]heptadiene, 1,5-cyclooctadiene, propene, dicyclopentadiene, and cycloheptatriene to give 9 η-olefin complexes, e.g. [MLL₁][PF₆]₂ (L₁ = η-cyclooctadienyl, 1,2,3,4,5-η-6-acetonyl cycloheptadienyl) which were characterized by anal. and NMR data. The olefins were deprotonated by [ML(Me₂CO)₃][PF₆]₂, except for cycloheptadiene, which underwent nucleophilic attack by the solvent with [ML(XH)_n][PF₆]₂ (XH = Me₂CO, M = Rh, Ir; XH = MeOH, M = Rh) to give [MLL₂][PF₆] (L₂ = 6-exo-acetonyl-, 6-exo-methoxy-1,2,3,4,5-η-cycloheptadienyl). The ¹³C and ¹H NMR spectra are reported and discussed.

L5 ANSWER 28 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1971:3721 CAPLUS

DN 74:3721

TI Pentamethylcyclopentadienyl-rhodium and -iridium halides. II. Reactions with mono-, di-, and triolefins

AU Maitlis, Peter M.; Moseley, K.; Kang, Jung W.

CS Dep. Chem., McMaster Univ., Hamilton, ON, Can.

SO Journal of the Chemical Society [Section] A: Inorganic, Physical, Theoretical (1970), (17), 2875-83

CODEN: JCSIAP; ISSN: 0022-4944

DT Journal

LA English

AB Dimeric dichloropentamethylcyclopentadienylrhodium and -iridium complexes, [M(C₅Me₅)Cl₂]₂ (M = Ir, Rh), reacted in ethanol in the presence of Na₂CO₃ with butadiene, cycloheptatriene, and 6,6-diphenylfulvene, giving pentamethylcyclopentadienylrhodium(III) or -iridium(III) complexes of π-1-methylallyl, π-cyclohepta-2,4-dienyl, and (1,1-diphenylmethyl)cyclopentadienyl. Under similar conditions with [Rh(C₅Me₅)Cl₂]₂, norbornadiene and dicyclopentadiene gave pentamethylcyclopentadienylrhodium(I) diene complexes: ethylene gave bis(ethylene)rhodium(I) and -iridium(I) complexes. A hydrido-intermediate is implied in these reactions and both the hydrido- and deuteriochloro(triphenylphosphine)pentamethylcyclopentadienyliridium complexes were isolated and characterized. With cyclopentadiene, [Rh(C₅Me₅)Cl₂]₂ gave the cation and (cyclopentadienyl)-endo-H-pentamethylcyclopentadienylrhodium(I). (Cyclopentadienyl)-exo-H-pentamethylcyclopentadienylrhodium(I) was obtained by reduction of [Rh(C₅Me₅)(C₅H₅)]⁺ with NaBH₄ and was much more reactive than the endo-H-isomer. With halogenating agents, [Rh(C₅Me₅)(C₅H₅)]⁺ was the product, whereas the endo-H-isomer underwent cleavage to [Rh(C₅Me₅)X₂]₂ and [Rh(C₅H₅)X₂]₂. [Ir(C₅Me₅)Cl₂]₂ reacted with cyclopentadiene to give only the [Ir(C₅Me₅)(C₅H₅)]⁺ cation, which on reduction gave exo-H-Ir(C₅Me₅H)(C₅H₅) and Ir(C₅Me₅)(C₅H₆).